equilibrium constant of ca. 0.38 was obtained. This suggests that the reactivity (or nucleophilicity) of N_3^- and OH^- toward Ag(III) is similar.

Thiosulfate[20] has an equilibrium constant for complexation with $Ag(OH)_4^-$ 4 orders of magnitude greater than that obtained here. This further suggests that OH^- and N_3^- are relatively poor nucleophiles for Ag(III), with the order of nucleophilicity being $S_2O_3^{2-} >> OH^- \geq N_3^-$. The same order has been observed for Pd(II), which is isoelectronic with Ag(III). Thus, the appearance of both ligand and solvent paths in this system and an equilibrium constant near unity are not unexpected.

The rates of OH^- substitution in $Ag(OH)_4^-$ has been determined for a variety of substrates including thiosulfate,[20] periodate,[22], tellurate[22] and ethylenediamine.[19] A wide range of substitution rates has been observed that parallels that found for Pd(II). The largest rate constants have been obtained for the softer[23] ligands such as thiosulfate (ca. 10^4 M^{-1} s^{-1}), whereas the slowest substitution rates have been observed for relatively hard ligands such as azide ion ($k_6 = 7.3$ M^{-1} s^{-1}).

The mechanism proposed for the reduction of silver(III) by azide ion (eq 13–17) involves reaction of the intermediate azido complex with a second molecule of azide. Under the conditions of this study, this occurs by two parallel paths. These reactions may involve either five-coordinate intermediate (eq 13–15) or ligand replacement (eq 16–17). Previous studies have shown that electron transfer within a five-coordinate intermediate can occur in silver(III) reactions.[19,24,25] However, since formation of both *cis*- and *trans*-diazido complexes would also be expected, neither alternative can be eliminated. In any case, the most striking feature for both parts of the redox mechanism is that adjacent azides seem to be required for electron transfer. This suggests a transition state involving a seven-membered cyclic Ag–N_6 species and/or a neutral N_6 molecule. This would allow for the direct formation of Ag(I) and nitrogen, consistent with the product analysis, EPR, and polymerization experiments. A recent study[11] of the decomposition of *cis*-$Pt(N_3)_2(PPh_3)_2$ has, indeed, provided spectral evidence for the intermediate formation of neutral cyclic hexazine, N_6.

Kinetic studies of the reaction of HN_3 with the aquametal ions of Mn(III),[1-3] Co(III),[4-6] and Ce(IV)[7] have given rise to several postulated mechanisms and a certain amount of controversy. For example, both $N_3\cdot$ and $H_2N_6^{+}\cdot$ have been suggested as intermediates in the Co(III) system under comparable conditions. The Mn(III) reaction seems to involve either a one-electron or two-electron mechanism (involving a Mn(IV) intermediate) depending on [HN_3]. The outer-sphere reductions of $Ni(bpy)_3^{3+}$[26] and $Co(Me_6[14]\ diene)^{3+}$[27] involve direct N_3^- (even in acid media) oxidation to $N_3\cdot$. In spite of the high thermodynamic instability of N_3^- relative to N_2, the reaction of $Ag(OH)_4^-$ with N_3^- is one of the slowest studied to date. Indeed, under comparable [azide] (HN_3 or N_3^-), it is slower than any of the above reactions, all of which were studied in acid media. Furthermore, the overall redox rate in this system has no detectable contribution from the unimolecular decomposition of $Ag(OH)_3N_3^-$. Our observations suggest that the presence of two adjacent molecules of N_3^- in the activated complex facilitates electron transfer by offering a path with a smaller energy barrier than required for the formation of $N_3\cdot$.

Nevertheless, in contrast to the reaction with hydrogen peroxide,[24] the two-electron reduction of Ag(III) by N_3^- is a relatively slow reaction since some degree of electronic rearrangement and formation of a N–N bond is still necessary.

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Notes

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Unusual EPR Spectrum of $[CuCl_2(H_2O)_2][(C_6H_5)_3PO]_4$: Effect of Magnetic Dipole Coupling with Slow Electron Exchange

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EPR spectroscopy provides a powerful method of investigating metal–ligand bonding and magnetic interactions in transition-metal complexes. Most work in the latter area has involved dimers in which the unpaired electrons exchange between the metal ions more rapidly than on the EPR time scale. In the case of the most widely studied metal, copper(II), sophisticated computer simulation programs have been developed to investigate the way in which the characteristic seven-line spectra of such systems depend upon factors such as the metal–metal separation and the relative orientation of the complexes in the dimer.[1] Magnetic dipole interactions can also significantly affect EPR spectra even when the rate of electron exchange is relatively slow; it is interactions of this type that produce the relatively broad lines observed for pure, as opposed to magnetically dilute, compounds.[2] When the crystal structure of a pure compound is such that each metal has only a few paramagnetic neighbors, magnetic dipole splittings of this kind may sometimes be resolved. Recently, the EPR spectra of single crystals of several copper(II) and vanadyl(IV) complexes have been interpreted in this manner.[3-7] The line shapes observed for these systems, which are quite different from those seen for dimers involving rapid electron exchange, are generally quite complex, ranging from five[5] to nine[6,7] lines in the case of the copper(II) compounds, with the

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0020-1669/84/1323-2359$01.50/0

pattern being strongly influenced by the number of nearest neighbors and the relative magnitudes of the magnetic dipole and hyperfine interactions.

As part of a general investigation of the electronic structures of chlorocuprate complexes,[8,9] we recently measured the EPR spectra of single crystals of $[CuCl_2(H_2O)_2][(C_6H_5)_3PO]_4$. This compound contains isolated, planar *trans*-$CuCl_2(H_2O)_2$ complexes, with each water ligand hydrogen bonded to two $(C_6H_5)_3PO$ molecules.[10] In addition to providing information on the metal–ligand bonding interactions of the aqua and chloro ligands, the spectrum showed evidence of magnetic dipole coupling between neighboring molecules in the crystal, and this note presents the results of this study.

Experimental Section

Single crystals of $[CuCl_2(H_2O)_2][(C_6H_5)_3PO]_4$ were prepared as described previously,[10] and the room-temperature EPR spectra of several crystals were recorded at X-band frequency, with a JEOL FE-3X spectrometer for rotations of the magnetic field in the (001), (010), and bc^* crystal planes. The monoclinic unit cell of the compound (space group $P2_1/c$, $Z = 2$, $a = 14.038$ Å, $b = 9.826$ Å, $c = 27.544$ Å, $\beta = 122.54°$) contains two $CuCl_2(H_2O)_2$ molecules, and overlapping of the signals due to these molecules precluded the measurement of g values except when the magnetic field was parallel and perpendicular to the b crystal axis. The g values obtained from two separate crystals are listed in Supplementary Table I, and these were used to derive the molecular values $g_x = 2.049$ (1), $g_y = 2.081$ (1), and $g_z = 2.269$ (1) by a method described previously,[11] the estimated error limits being given in parentheses. The molecular z axis was defined perpendicular to the plane formed by the copper and the oxygen and chlorine ligand atoms, and within experimental error the principal x and y axes of the g tensor were found to lie parallel to the Cu–O and Cu–Cl bond directions, respectively.

Discussion

Effect of Magnetic Dipole Coupling. In general, a single, broad line was observed for rotation of the crystal in the (010) plane, and two overlapping lines were observed for the (100) and bc^* rotations. When the magnetic field was parallel to the b crystal axis, however, the spectrum consisted of four lines separated by $\sim 1.7 \times 10^{-3}$ T, each split into three components (Figure 1A). The spectrum was also measured at 77 K for this orientation of the magnetic field, but no improvement in resolution occurred. The basic four-line pattern clearly results from the copper hyperfine interaction and shows that the rate of electron exchange between the metal ions is slower than the hyperfine splitting expressed in frequency units (i.e. less than $\sim 10^9$ s^{-1}; rapid electron exchange over all the copper(II) ions located along the b axis would produce a single "exchange-narrowed" line[12]). The splitting of each of these lines is assigned to a dipolar coupling with the unpaired electron spins of the two neighboring copper(II) ions at ±1 unit cell length along the b crystal axis. This should produce three components of intensity 1:2:1, with the splitting d between the central and outer peaks being given by the expression[13] appropriate to two point-dipoles separated by a distance r:

$$d = Cg(1 - 3\cos^2\theta)/r^3 \qquad (1)$$

Here, g is the g value of the complex and θ is the angle between the magnetic field direction and the interdipole vector, this being 0° in the present situation. If d is measured in T and r in Å, the constant C takes the value 0.927.

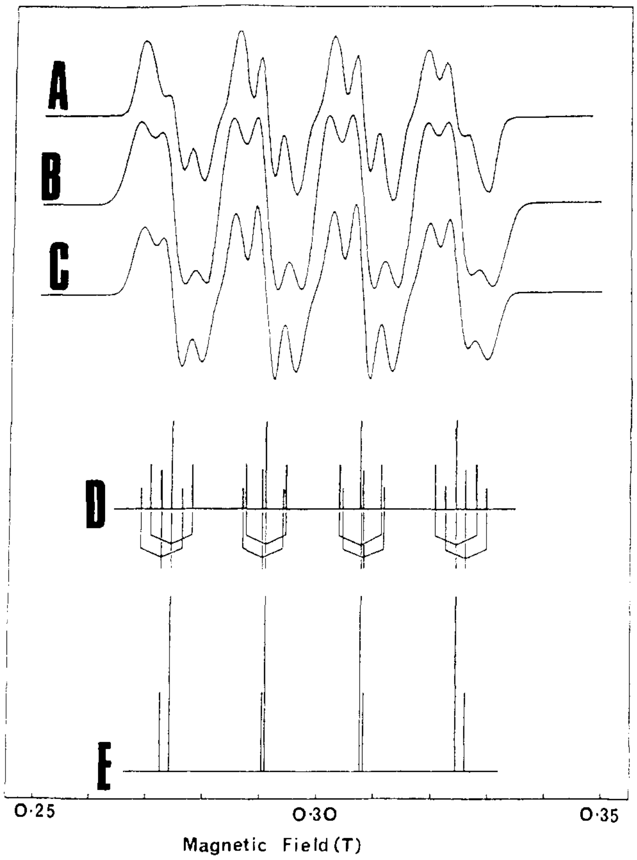

Figure 1. (A) Observed EPR spectrum. (B) Spectrum simulated by assuming dipole interaction $d = 4.4 \times 10^{-3}$ T. (C) Spectrum simulated by assuming $d = 3.7 \times 10^{-3}$ T. (D) "Stick" diagram showing line positions in (C). (E) Line positions neglecting dipole–dipole interaction.

The expected splitting pattern is illustrated in "stick" form in Figure 1D,E, including also the slightly different hyperfine splitting parameters of the two copper isotopes.[5] Assuming a dipolar splitting $d = 4.4 \times 10^{-3}$ T, as predicted by eq 1, and using the value $r = 9.93$ Å, suggested by the crystal structure determination, and the value $g = 2.254$, measured when the magnetic field was parallel to b, yield a simulated EPR spectrum in reasonable agreement with experiment (Figure 1B). A Gaussian line shape[5] was used in the simulation, and the half-width was taken to be 2.0×10^{-3} T. However, optimum agreement with the observed spectrum was obtained by assuming a dipolar splitting $d = (3.7 \pm 0.2) \times 10^{-3}$ T (Figure 1C) corresponding to an interdipolar separation $r = 10.4 \pm 0.2$ Å from eq 1. It has been suggested[3,5] that a more realistic representation of the magnetic dipole interaction may be obtained by allowing first for delocalization of the unpaired electron density onto the ligand atoms and second for the spatial distribution of the $d_{x^2-y^2}$ orbital containing the bulk of the spin density. Assuming that 0.075 and 0.065 units of unpaired spin are localized at the position of each chloride and oxygen ligand, respectively,[14] and that the remaining 0.72 units are localized at points 0.5 Å along each direction of the x and y molecular axes, then eq 1 may be used to sum the dipolar interactions resulting from this charge distribution. The resulting estimate of 4.07×10^{-3} T is in reasonable agreement with the experimentally observed value of $(3.7 \pm 0.2) \times 10^{-3}$ T. This suggests that, as is the case with dimers involving rapid

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[13] See ref 2, p 524, eq 9.62; note that d (tesla) $\propto$ d (energy units)/g.

[14] These approximate estimates of the covalences of the Cu–OH_2 and Cu–Cl bonds are based upon analysis of the metal–ligand superhyperfine interactions. See: Getz, D.; Silver, B. L. *Inorg. Chem.* **1976**, *15*, 1240. Deeth, R. J.; Hitchman, M. A.; Lehmann, G.; Sachs, H. *Ibid.*, in press, and references therein.

electron exchange,[1] the splittings caused by magnetic dipole interactions where the electron exchange between the coupled metal ions is relatively slow also have the potential to provide quite accurate estimates of the metal–metal separation.

Interpretation of the *g* Values of the Complex. For a complex of rhombic symmetry such as $CuCl_2(H_2O)_2$, to a first approximation the molecular *g* values are related to the excited-state energies E_{xz}, E_{yz}, and E_{xy} by the expressions[11]

$$g_x = 2.002 - 2\lambda k_\perp^2(a - 3^{1/2}b)^2/E_{yz} \tag{2a}$$

$$g_y = 2.002 - 2\lambda k_\perp^2(a + 3^{1/2}b)^2/E_{xz} \tag{2b}$$

$$g_z = 2.002 - 8\lambda k_\parallel^2 a^2/E_{xy} \tag{2c}$$

The constants *a* and *b* in these equations define the proportions of the $d_{x^2-y^2}$ and d_{z^2} orbitals in the ground-state wave function, which is of the form $ad_{x^2-y^2} - bd_{z^2}$. Substitution into eq 2a–c of $\lambda = -828$ cm^{-1}, together with the observed molecular values $g_x = 2.049$, $g_y = 2.081$, and $g_z = 2.269$ and excited-state energies $E_{xy} = 13\,400$ cm^{-1}, $E_{xz} = 14\,500$ cm^{-1}, and $E_{yz} = 14\,600$ cm^{-1} obtained from the electronic spectrum of the complex,[15] yields the orbital reduction parameters $k_\parallel^2 = 0.54$ and $k_\perp^2 = 0.55$ and a value $b = 0.074$ for the mixing coefficient of the d_{z^2} orbital in the ground-state wave function. As expected, the orbital reduction parameters lie approximately midway between the values of ~0.65 and ~0.4 observed for the $Cu(H_2O)_6^{2+}$ [11] and $CuCl_4^{2-}$ ions,[8] respectively. It should be noted that this approach considers that the in-plane *g* anisotropy is dominated by the difference in the metal–ligand perturbation along the *x* and *y* axes. In effect, this assumes that any differences in the contributions from the ligand parts of the ground-state wave functions are insignificant. In the case of the axially symmetric planar $CuCl_4^{2-}$ ion calculations suggest that the net contribution to the *g* shift due to the orbital angular momentum associated with the ligand part of the ground-state wave function is quite small,[16] but this is largely because of the cancellation of significant terms derived by including charge-transfer excited states and ligand spin–orbit coupling effects. It must be stressed that it is not clear to what extent the different covalencies of the Cu–O and Cu–Cl bonds will affect the *g* anisotropy in a mixed-ligand complex such as $CuCl_2(H_2O)_2$, so that the present interpretation must be viewed with caution.

Simple theory suggests that *b* should be related to the difference in the σ perturbation produced by the ligands along the *x* and *y* axes. It is known that H_2O lies slightly higher in the spectrochemical series than Cl^- when bonded to a first-row transition-metal ion, but measurements made on octahedral complexes cannot distinguish between the contributions made by σ and π bonding to the overall ligand field splitting.[17] The fact that *b* is positive in $CuCl_2(H_2O)_2$, with g_x being parallel to the $Cu-OH_2$ bond directions, suggests that water is a stronger σ donor than chloride toward copper(II).[18] The angular-overlap model provides a useful way of quantifying metal–ligand interactions, and this suggests[19] that in a planar complex such as *trans*-$CuCl_2(H_2O)_2$

$$b \approx \tfrac{1}{2}(3^{1/2})(e_{\sigma x} - e_{\sigma y})/(e_{\sigma x} + e_{\sigma y}) \tag{3}$$

Here, $e_{\sigma x}$ and $e_{\sigma y}$ represent the σ-antibonding perturbations due to one water and one chloride ligand, respectively. These perturbations are related to the diatomic overlap integrals S_σ between the metal d and ligand p orbitals by the expression $e_\sigma = KS_\sigma^2$, where *K* is a constant.[11] Studies of the electronic spectra of a range of chlorocuprate(II)[8] and hexaaquocuprate(II)[11] complexes suggest that $K_\sigma(H_2O) \simeq 8.6 \times 10^5$ cm^{-1} and $K_\sigma(Cl^-) \simeq 9.4 \times 10^5$ cm^{-1}, and these values, together with the diatomic overlap integrals[20] $S_\sigma = 0.094$ and $S_\sigma = 0.083$ appropriate to the bond distances Cu–O = 1.90 Å and Cu–Cl = 2.23 Å in $[CuCl_2(H_2O)_2][(C_6H_5)_3PO]_4$,[10] yield the parameters $e_{\sigma x} = 7600$ cm^{-1} and $e_{\sigma y} = 6475$ cm^{-1}. Substitution of these values into eq 3 suggests a mixing coefficient $b = 0.069$ in good agreement with the value $b = 0.074$ obtained from the EPR parameters. While it must be emphasized that the agreement may be purely fortuitous, the self-consistency of the results is gratifying and suggests that the angular-overlap model holds considerable promise as a means of parametrizing the metal–ligand interactions in low-symmetry metal complexes, such as those that are often present in molecules of biological importance.

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Registry No. $[CuCl_2(H_2O)_2][(C_6H_5)_3PO]_4$, 72268-10-1.

Supplementary Material Available: A listing of the crystal *g* values for $[CuCl_2(H_2O)_2][(C_6H_5)_3PO]_4$ (1 page). Ordering information is given on any current masthead page.

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Ligand–Metal Interrelationships. 2. Effect of the Change from Square-Planar to Octahedral Coordination on the pK_a of the Ligand in Unsaturated Tetraaza Macrocyclic Nickel Complexes: A Pulse-Radiolytic Study

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We have recently reported that the pK_a of the macrocylic ligand in the tervalent nickel complex of 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,13-diene, NiL_1^{3+}, is higher than the pK_a measured for the divalent complex, NiL_1^{2+}.[1] This surprising result, in view of the greater acidity expected for the tervalent nickel complex, was explained by the observation that the pK_a predicted for the ligand in this complex coincides with the pH range in which two hydroxyl groups are axially coordinated to the nickel. Thus, the results only indicate that $Ni(OH)_2^+$ has a smaller effect on the ligand pK_a than does Ni^{2+}. In addition, we had tentatively assigned the strong absorption, $\lambda_{max} = 600$ nm, observed for the alkaline form of the tervalent complex as a ligand-to-metal charge-transfer transition.[1]

In order to confirm these conclusions we examined the nickel complex of 11-methyl-13-(trifluoromethyl)-1,4,7,10-tetraazacyclotrideca-10,13-diene, NiL_2^{3+}. It was observed that the trifluoromethyl group sufficiently stabilizes the alkaline form

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